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Iridoid glucosides in the genus *Veronica* (Plantaginaceae) from New Zealand

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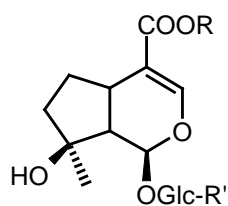
A B S T R A C T

Four simple iridoid glucosides, three known esters of catalpol, seven esters of aucubin, and two phenylethanoids were isolated from *Veronica hookeri* (syn. *Hebe ciliolata*; Plantaginaceae). Of these, none of four aromatic (*p*-methoxybenzoyl, isovanilloyl, veratroyl, caffeoyl) 6-*O*-esters of aucubin and 6''-*O*-benzoyl mussaenosidic acid, had been reported from nature before. Similarly, three simple iridoid glucosides, two esters of 6-*O*-rhamnopyranosylcatalpol, and two phenylethanoid glucosides, as well as 1-*O*-benzoyl-3- α -glucuronosylglycerol, and 1-*O*- β -benzoyl rutinose were isolated from *Veronica pinguifolia* (syn. *Hebe pinguifolia*). The compound 3''-*O*-benzoyl-2''-*O*-caffeoyl 6-*O*-rhamnopyranosylcatalpol had not been reported previously. The pattern of the structural features of the iridoid glucosides is overlaid onto the latest molecular phylogenetic framework of *Veronica* sects. *Hebe* and *Labiatooides*, and discussed in the context of evolutionary trends.

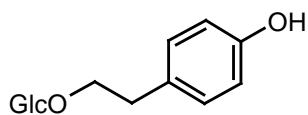
§ PK-M and KDP contributed equally to this work.

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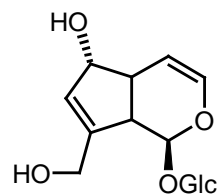
E-mail address: srj@kemi.dtu.dk (S.R. Jensen).



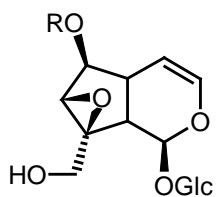
1; R=R'=H
1a; R=Me; R'=H
1b; R=H; R'=6'-O-Benzoyl



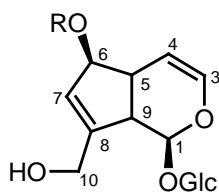
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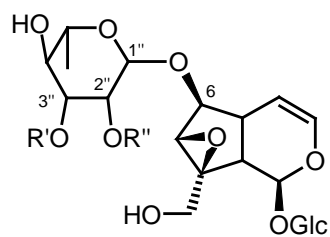
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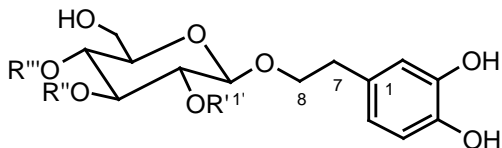
4; R=H; Catalpol
4a; R=Vanilloyl
4b; R=Caffeoyl
4c; R=isoFeruloyl



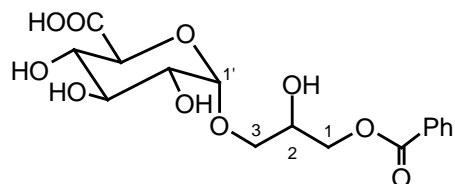
5; R=H; Aucubin
5a; R=Benzoyl
5b; R=p-OH-Benzoyl
5c; R=p-OMe-Benzoyl
5d; R=3,4-diOH-Benzoyl
5e; R=Vanilloyl
5f; R=isoVanilloyl
5g; R=3,4-diOMe-Benzoyl
5h; R=Caffeoyl



6; R'=R''=H
6a; R'=Caffeoyl; R''=H
6b; R'=Benzoyl; R''=Caffeoyl



7a; R'=H; R''=Rha; R'''=Caffeoyl
7b; R'=Ara; R''=Rha; R'''=Caffeoyl
7c; R'=Xyl; R''=Rha; R'''=Caffeoyl



8; 1-O-Benzoyl-3- α -glucuronosyl-glycerol

List of Supporting Information

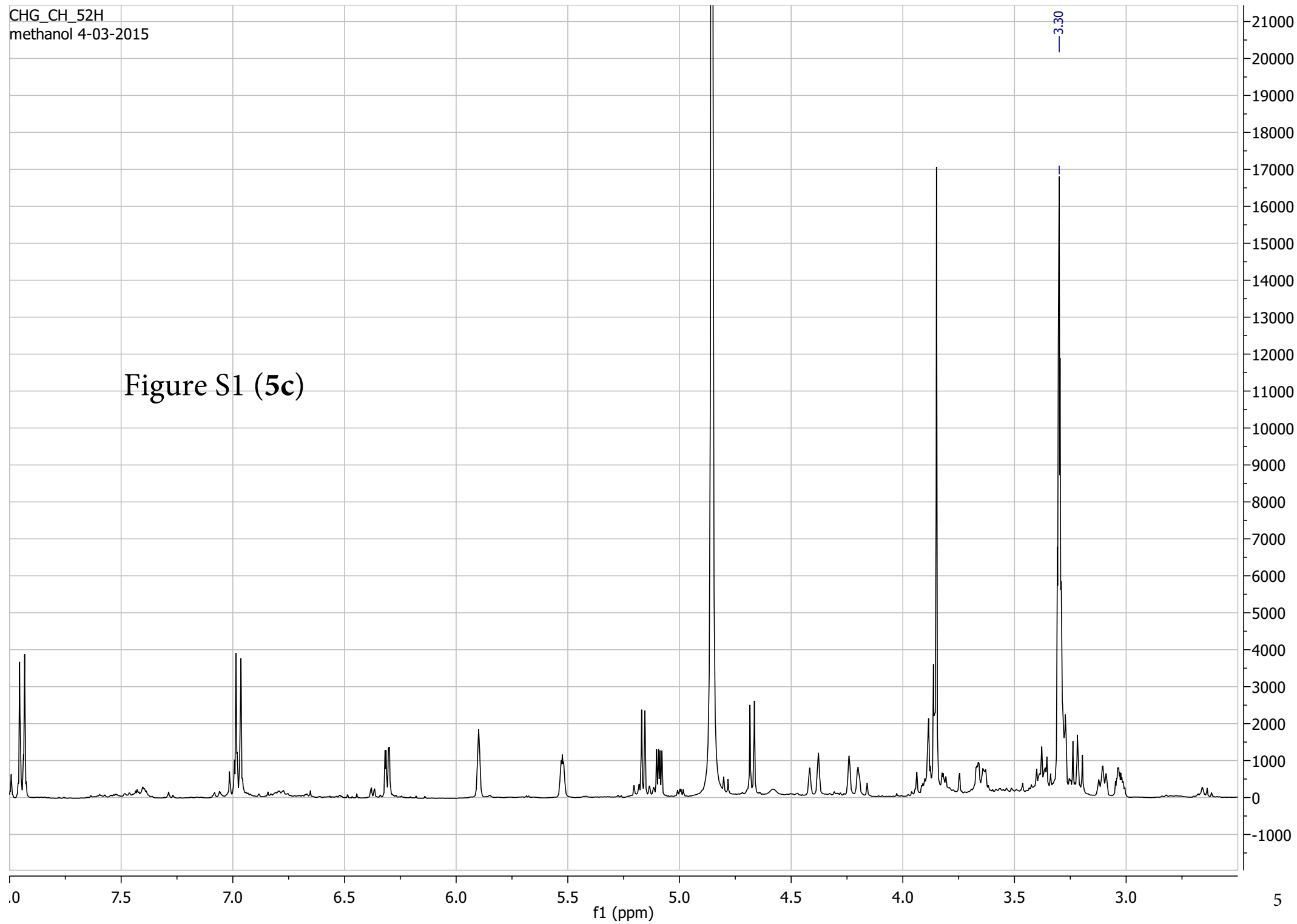
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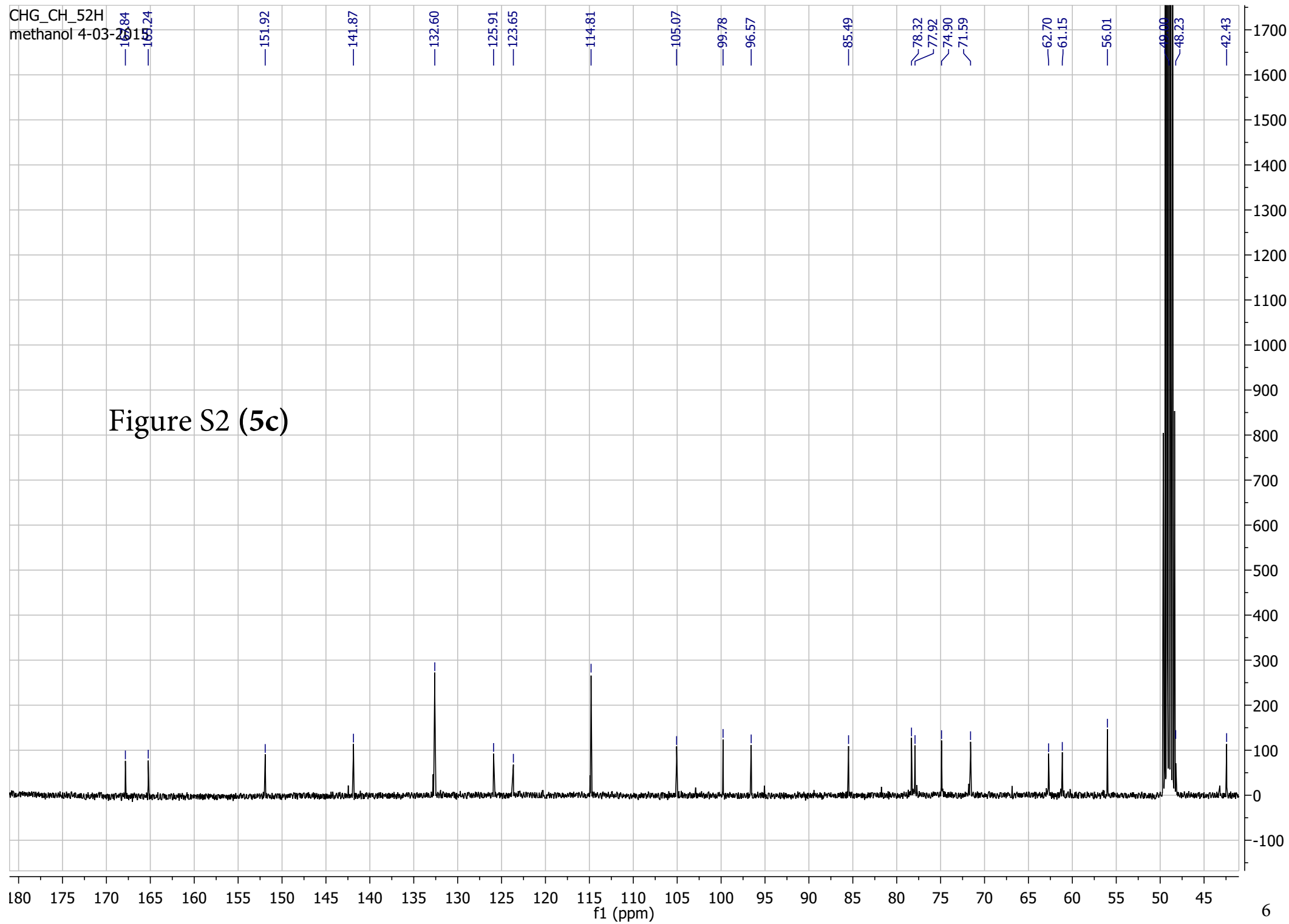
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Table SII. GenBank numbers of ITS-sequences used in the phylogenetic analysis

Species	GenBank number
<i>V. brachysiphon</i> (Summerh.) Bean	KJ630628
<i>V. buchananii</i> Hook. f.	KJ630629
<i>V. catarractae</i> G. Forst.	AY034859
<i>V. cheesemanii</i> Benth.	AF229046
<i>V. ciliolata</i> (Hook. f.) Garn.-Jones	AF229037
<i>V. cupressoides</i> Hook. f.	AF037378
<i>V. derwentiana</i> Andrews	JX193655
<i>V. elliptica</i> G. Forst.	AF037392
<i>V. hookeriana</i> Walp.	AY34860
<i>V. hulkeana</i> F. Muell.	AF037379
<i>V. lavaudiana</i> Raoul	AF229043
<i>V. ligustrifolia</i> R. Cunn.	KJ630647
<i>V. odora</i> Hook. f.	AF037388
<i>V. pentasepala</i> (L. B. Moore) Garn.-Jones	FJ848076
<i>V. perfoliata</i> R. Br.	JX196844
<i>V. pulvinaris</i> Hook. f.	AF229038
<i>V. raoulii</i> Hook. f.	AF037380
<i>V. salicifolia</i> G. Forst.	AF037385
<i>V. speciosa</i> A. Cunn.	AY034864
<i>V. stenophylla</i> Steud.	KJ630661
<i>V. thomsonii</i> (Buchanan) Cheeseman	AF229039
<i>V. topiaria</i> (L. B. Moore) Garn.-Jones	KJ630666

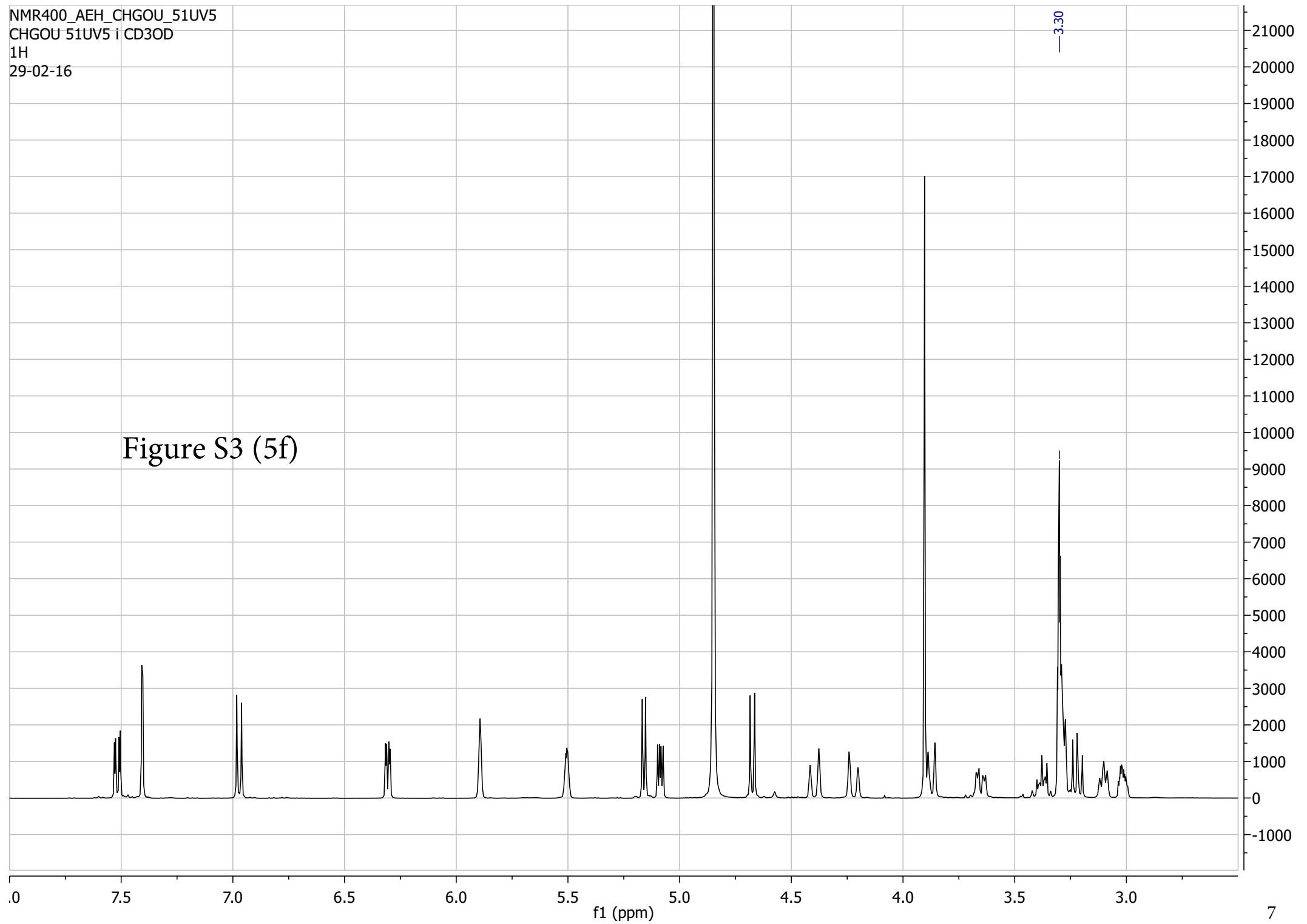
Figure S1 (5c)





NMR400_AEH_CHGOU_51UV5
CHGOU 51UV5 i CD3OD
1H
29-02-16

Figure S3 (5f)



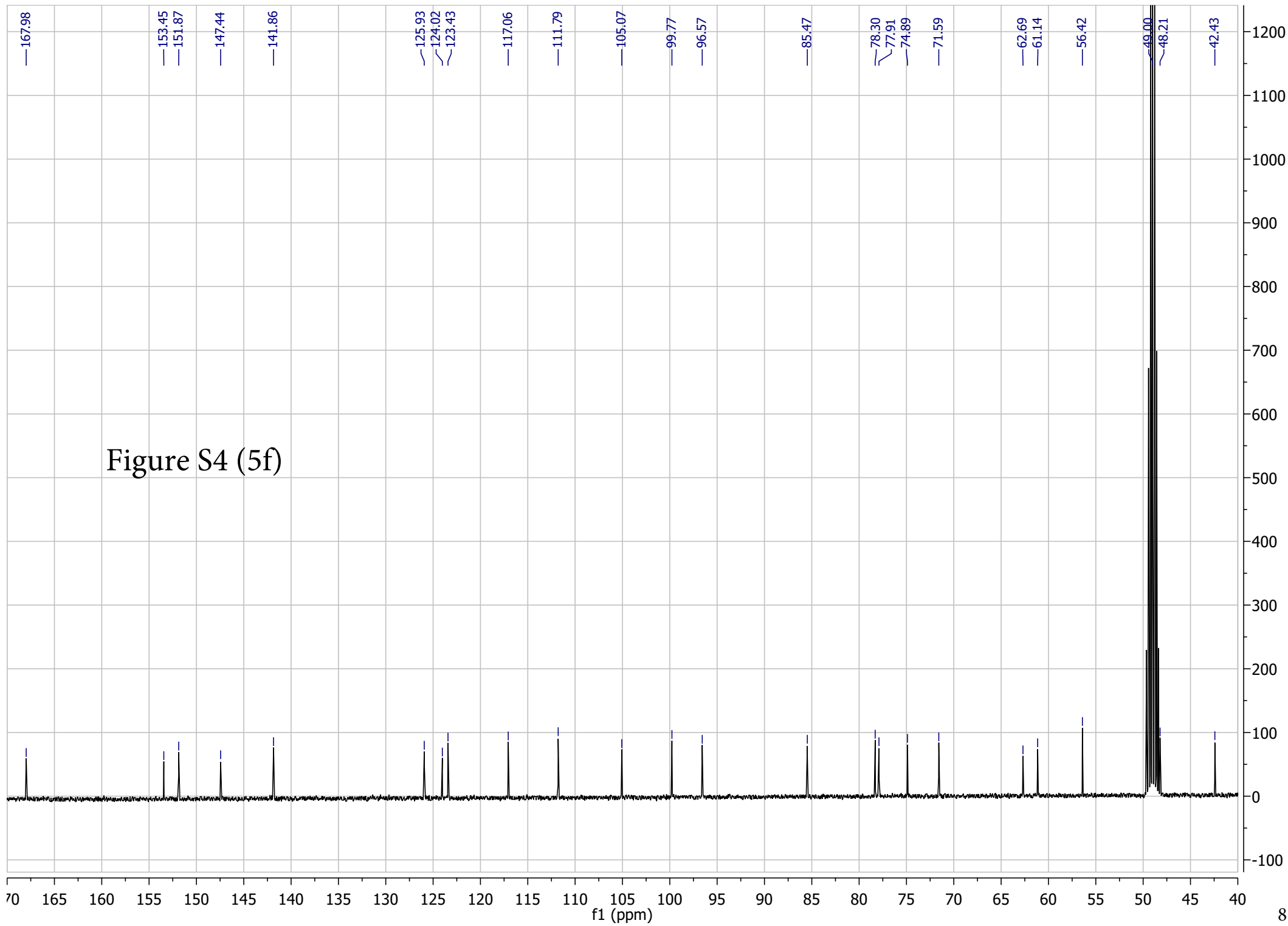
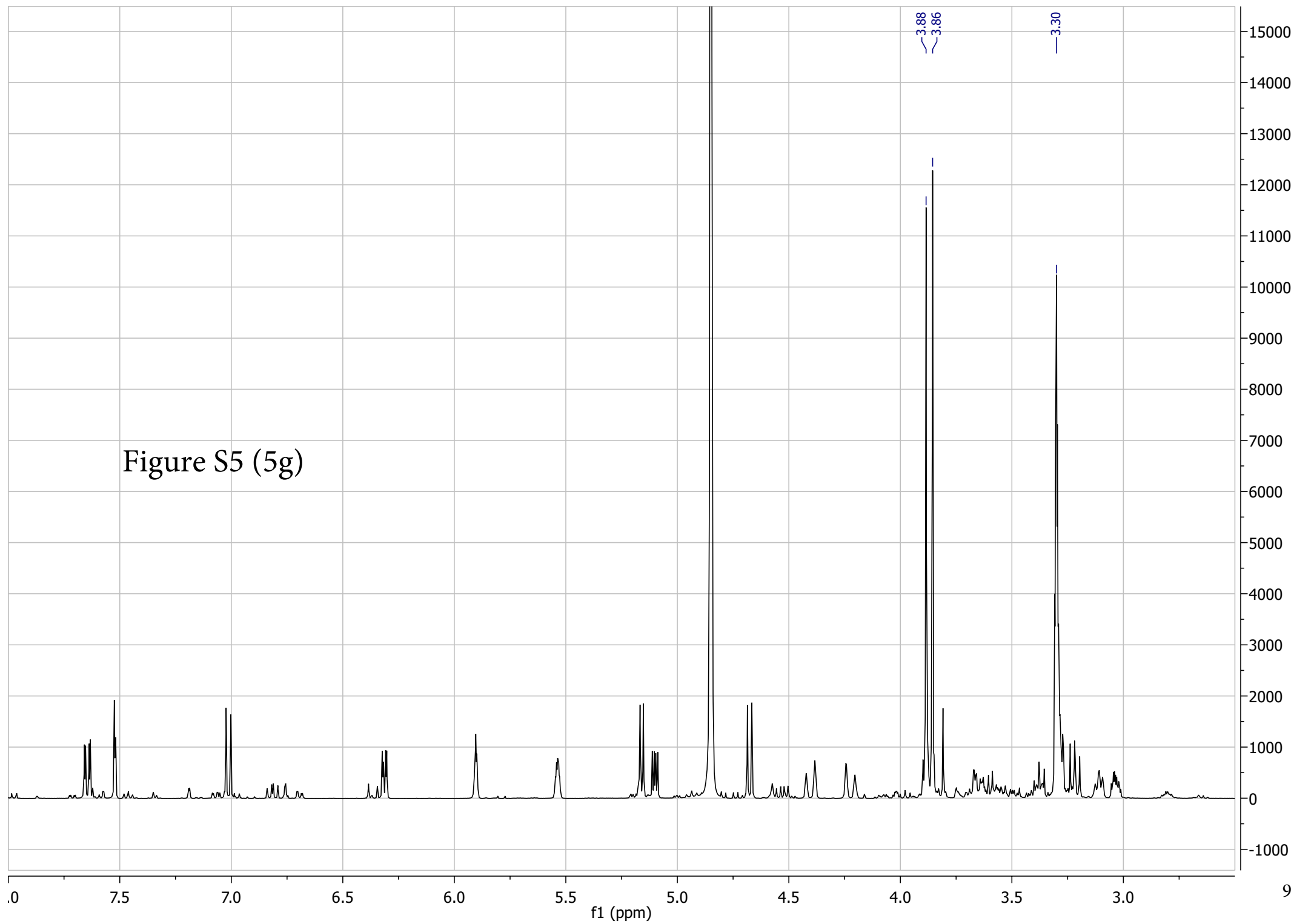
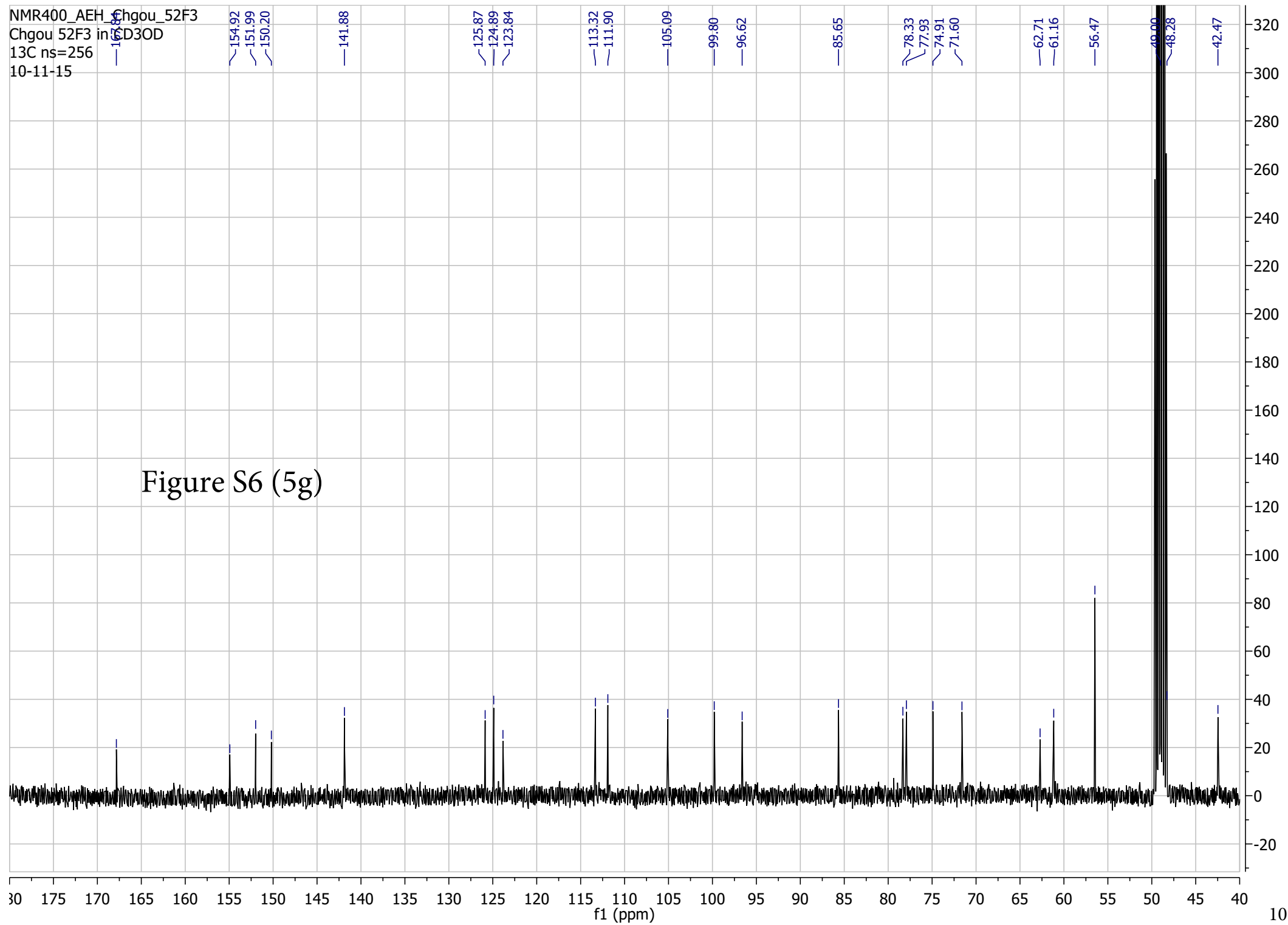


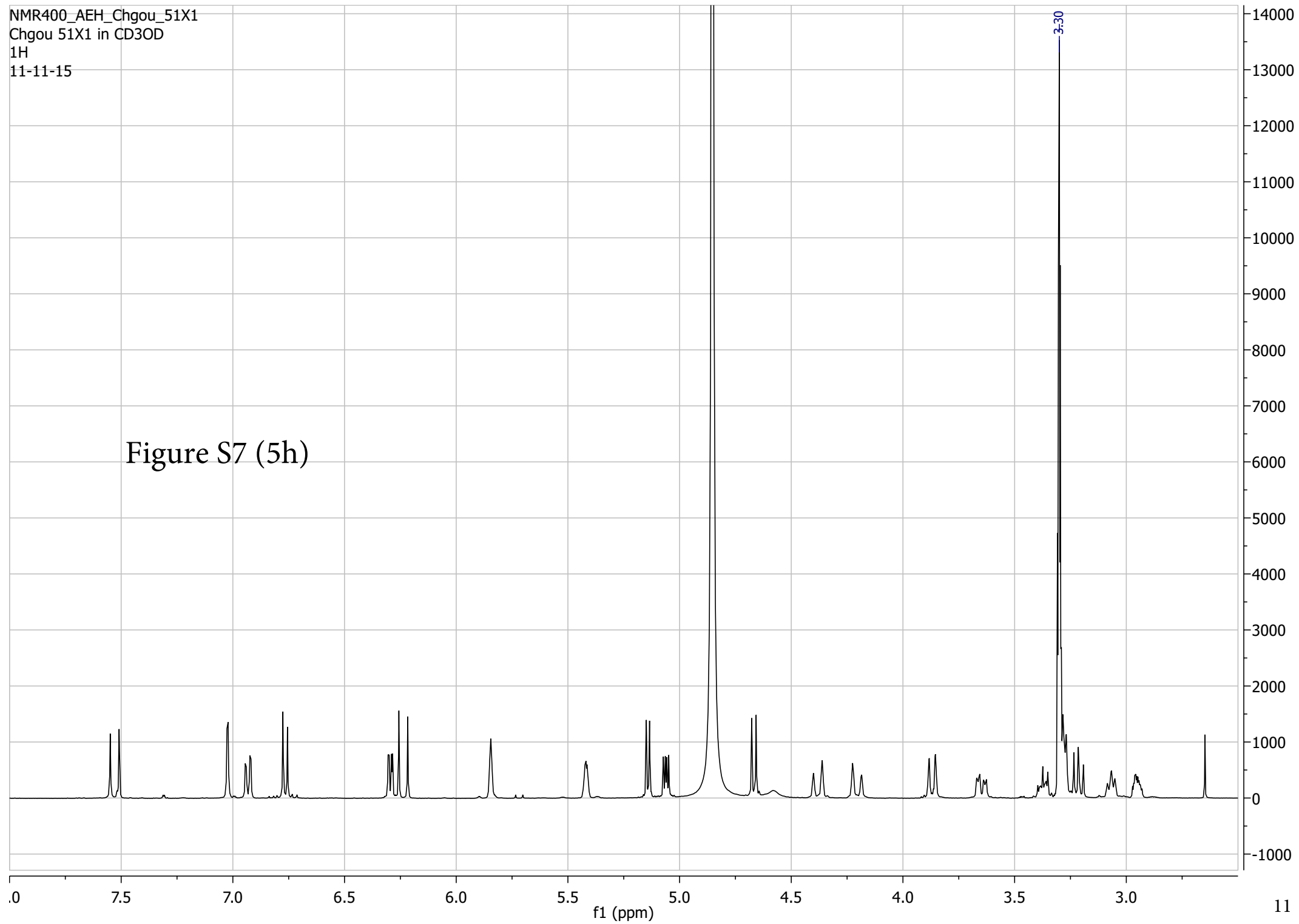
Figure S5 (5g)



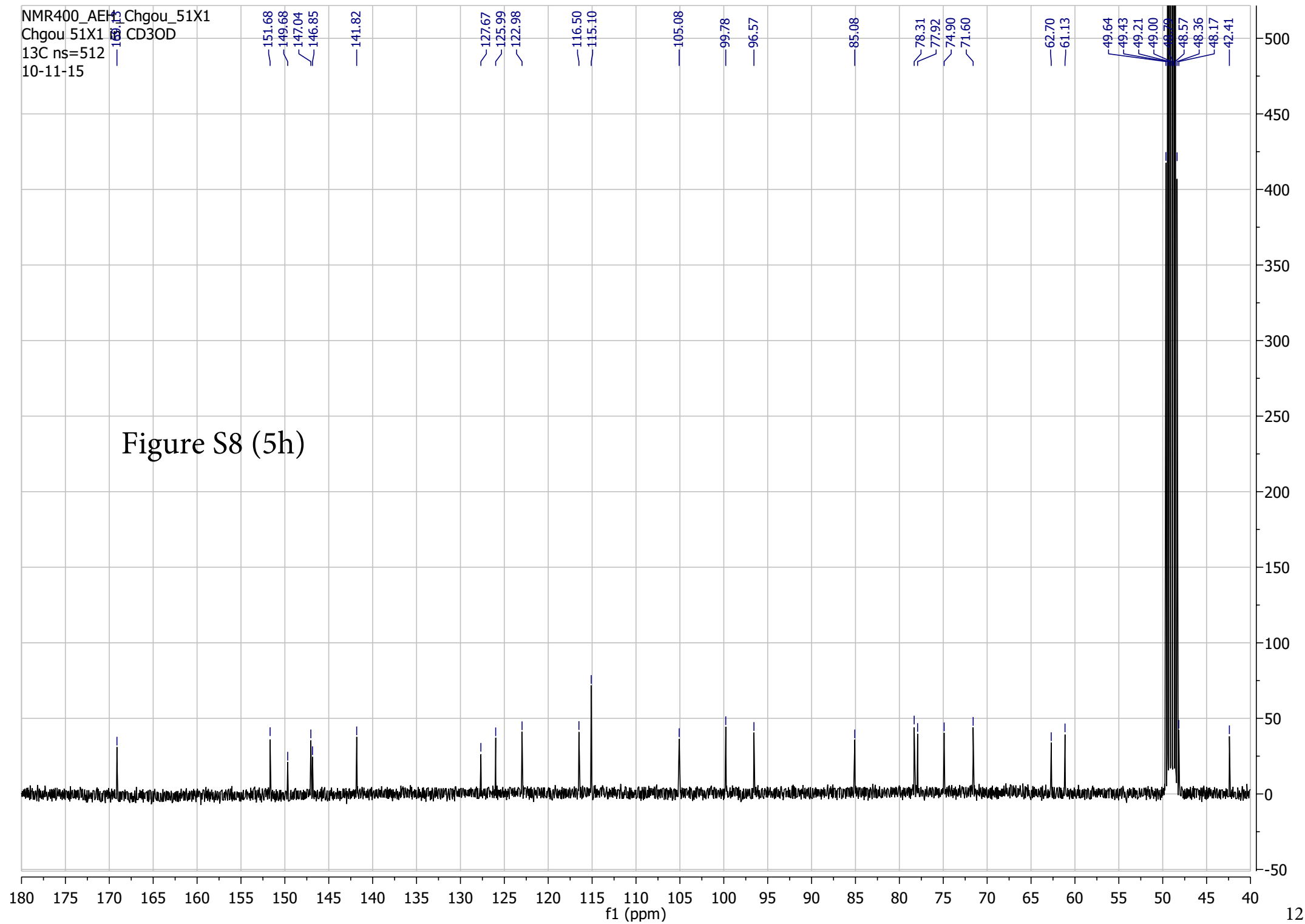


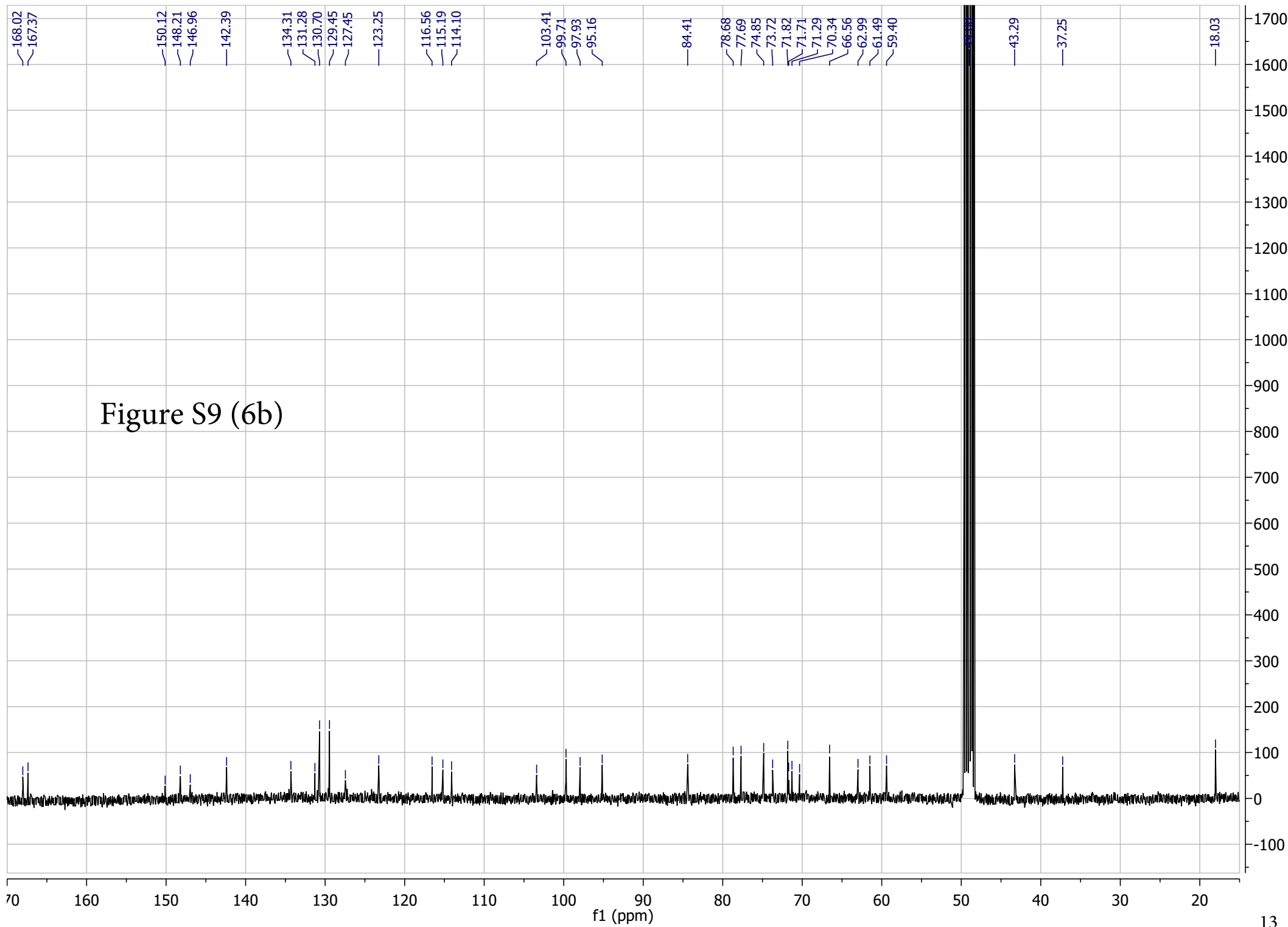
NMR400_AEH_Chgou_51X1
Chgou 51X1 in CD3OD
1H
11-11-15

Figure S7 (5h)



NMR400_AEH1 Chgou_51X1
Chgou 51X1 61 CD3OD
13C ns=512
10-11-15





NMR400_AEH_CHGOU_55NO5
CHGOU-55NO5 in CD3OD
1H ns=32
23-11-15

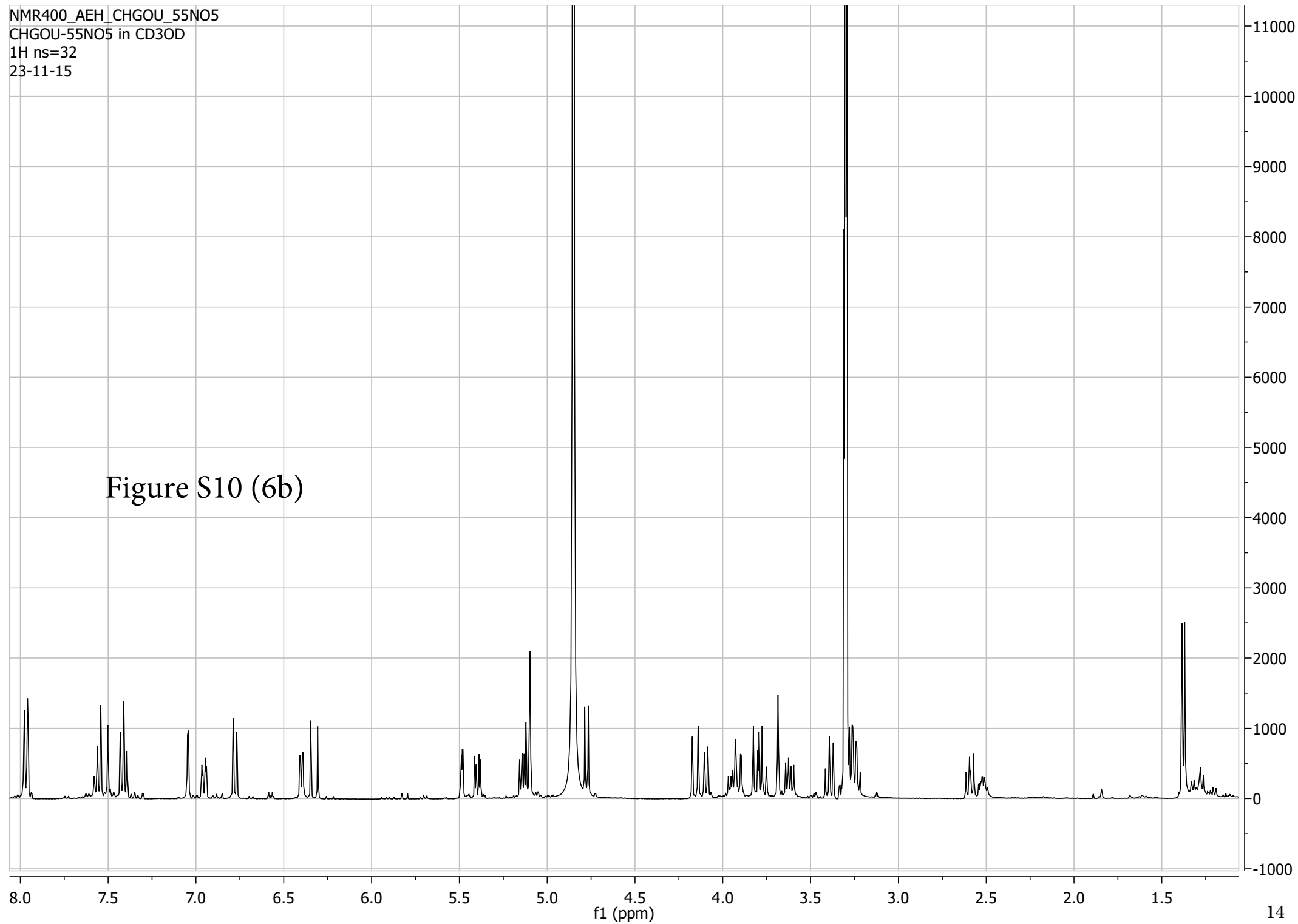


Figure S10 (6b)

NMR400_AEH_GHGOU_52F2
CHGOU 52F2 in CD3OD
1H
09-11-15

